

Verwey transition in Fe_3O_4 at high pressure: quantum critical behavior at the onset of metallization

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(Dated: February 6, 2008)

We provide evidence for the existence of a *quantum critical point* at the metallization of magnetite Fe_3O_4 at an applied pressure of $p_c \approx 8$ GPa. We show that the present ac magnetic susceptibility data support earlier resistivity data. The Verwey temperature scales with pressure $T_V \sim (1 - p/p_c)^\nu$, with $\nu \sim 1/3$. The resistivity data shows a temperature dependence $\rho(T) = \rho_0 + AT^n$, with $n \simeq 3$ above and 2.5 at the critical pressure, respectively. This difference in n with pressure is a sign of critical behavior at p_c . The magnetic susceptibility is smooth near the critical pressure, both at the Verwey transition and near the ferroelectric anomaly. A comparison with the critical behavior observed in the Mott-Hubbard and related systems is made.

PACS numbers: 71.30.+h, 71.27.+a, 05.70.Jk

Magnetite (Fe_3O_4) is among the oldest and most fascinating materials throughout the history of science. It is ferrimagnetic below the Curie temperature $T_C \approx 860$ K and semiconducting with a room temperature resistivity of $\rho(T = 300 \text{ K}) \simeq 10^{-2} \Omega\text{cm}$. The stoichiometric material undergoes a discontinuous Verwey transition¹ to a higher-resistivity phase at a temperature of $T_V \simeq (121 \pm 1)$ K, at which the resistivity at ambient pressure jumps up by about two orders of magnitude upon cooling. The transition is of a semiconductor-semiconductor type at lower pressures, although the exact difference between them remains somewhat elusive. In addition, the net magnetic moment has the value $\mu \simeq 4.1 \mu_B$ per formula and approximately corresponds to the spin $S = 2$ in Fe^{2+} high-spin configuration in the octahedral position (the remaining two Fe^{3+} ions, one in tetrahedral and one in the octahedral positions with spin $S = 5/2$ have their moments antialigned). The high-spin state is induced by Hund's rule coupling among $3d$ electrons.

Essential progress was made when samples with an extremely well controlled composition were synthesized² and studied.³ Notably, the change of the Verwey transition from first- to second-order has been discovered, depending on the off-stoichiometry parameter δ of $\text{Fe}_{3-\delta}\text{O}_4$. Also, the metallization of Fe_3O_4 has been achieved⁴ at a pressure of $p_c \simeq 8$ GPa.

The primary purpose of this work is to systematize the change in the properties of Fe_3O_4 with pressure and to single out universal features of these results. During the course of this work we reanalyzed the earlier resistivity data⁴ and have discovered that the combined magnetic susceptibility and resistivity data point to the possibility of a *quantum critical point* existing at the metallization threshold. This is explicitly verified by determining the pressure dependence of the critical exponents of both the transition temperature $T_V(p)$ and the resistivity just above the transition $\rho(T_{V+})$, as well as that of $\rho(T)$ at

the critical pressure and above it. Also, the pressure dependence of the two low-temperature anomalies in the ac susceptibility, presumably connected with the appearance of ferroelectricity, evolve with increasing pressure, but this aspect of the work will not be detailed here.

The importance of the presence of a quantum-critical-point (QCP) at the localization-delocalization boundary cannot be underestimated as there are no well defined *universality classes* as yet for this electronic transition. Previously, a *classical* critical point (of the Van der Waals-type) was determined⁵ in a three-dimensional system Cr-doped V_2O_3 , at $T_{crit} = 457.5$ K and $p_{crit} \simeq 3.7$ kbar, the existence of which was suggested earlier.⁶ The critical behavior in this case has the critical exponents of the mean-field type, as the T_{crit} value is rather high. Recently, a critical point has been seen⁷ in a quasi-two-dimensional organic solid at $T_{crit} = 39.7$ K and $p_c = 24.8$ MPa, with completely different critical exponents than those for the above three-dimensional case. A true quantum critical point (at $T = 0$) at the localization-delocalization boundary has been detected at the Kondo semiconductor - non-Fermi liquid boundary upon chemical substitution in $\text{CeRhSb}_{1-x}\text{Sn}_x$.⁸ In the last system, it is connected with the delocalization of $4f$ electrons due to Ce^{3+} and is induced by the change in carrier concentration upon doping. We suggest, that the present system (Fe_3O_4) represents the first example of a system with a true *quantum critical point* (with $T_{crit} = 0$) in a monocrystalline and stoichiometric system in a spin-polarized state, both in the semiconducting and the metallic states. In contrast, a different type of behavior has been observed^{9,10} in the antiferromagnetic system $\text{NiS}_{2-x}\text{Se}_x$, in which the Hund's rule coupling, leading to the high-spin $S = 1$ state in this case, also occurs. The differences are caused by a disparate magnetic ordering, as well as by the circumstance that, as we show, the metallic state of Fe_3O_4 is that of a *non-Fermi*

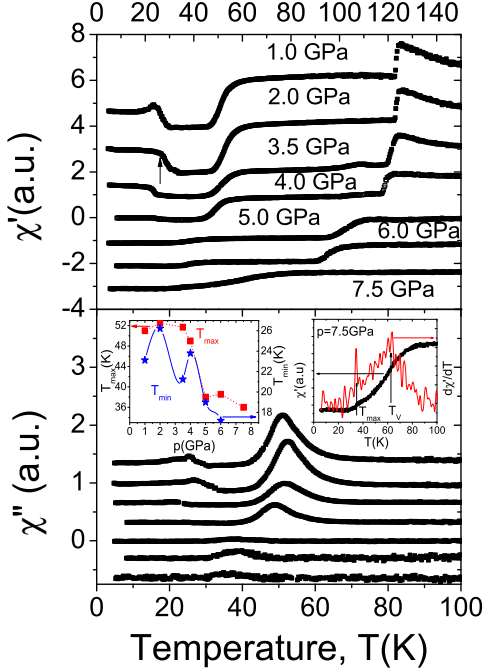


FIG. 1: Pressure dependence of ac magnetic susceptibility (at a frequency of 120Hz) for the stoichiometric single crystal; note different T scales for the real (χ') and the imaginary (χ'') parts of χ . Right inset: illustration of the definition of T_V from maximum of $d\chi'/dT$ when the sharp step in χ' was not observed (i.e. for $p > 3.5$ GPa). Left inset: T_{max} indicates the position of the anomaly near 50 K, whereas T_{min} the lower anomaly (indicated by the vertical arrow).

liquid, whereas that of $\text{NiS}_{2-x}\text{Se}_x$ is an almost localized antiferromagnetic Fermi liquid.

A single crystalline magnetic sample used for the ac magnetic susceptibility measurements, was cut from a larger crystal grown from the melt using the cold crucible technique (skull melter)², at Purdue University. The crystal was then annealed under CO/CO₂ gas mixtures to establish the stoichiometry² and rapidly quenched to room temperature to freeze in the high temperature thermodynamic equilibrium. Although this procedure generates octahedral defects, most of the low temperature electronic processes remain intact, as is evidenced by the sharp Verwey transition temperature T_V and the existence of the low temperature anomaly (observed only in the best crystals).

In Fig. 1 we display the temperature dependence of the ac susceptibility $\chi = \chi' + i\chi''$ components for selected pressures. The upper panel provides the real part χ' , for which three characteristic temperatures are: The Verwey temperature T_V (the uppermost jump), and the two temperatures associated with ferroelectricity,¹¹ for $T_{max} \sim 60 - 50$ K, and the lower anomaly at $T_{min} \sim 20$ K. With increasing pressure, all of them shift towards

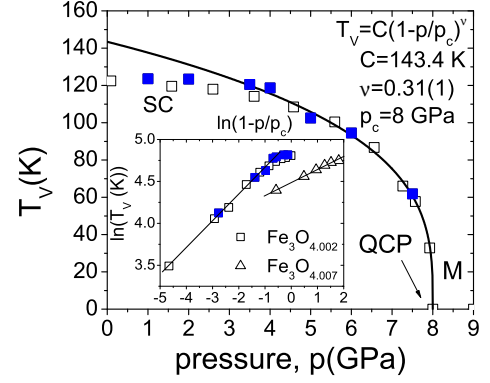


FIG. 2: Pressure dependence of the Verwey transition temperature T_V . We mark the data points from this work as solid squares (blue online) and those of Môri et al.⁴ by open squares. Solid line represents the fit specified and ending at quantum critical point (QCP). Inset: same in the doubly logarithmic scale. Open triangles show the respective critical behavior for slightly nonstoichiometric ($\delta = 0.007$) sample. M denotes a stable metallic state, whereas SC labels the semi-conducting state below T_V .

lower temperatures and eventually disappear for pressures $p \gtrsim 7.5$ GPa. Note that pronounced losses are observed near T_{max} . They are most probably due to the ferroelectric transition and associated with it ferroelectric domain dynamics. In the insets we mark the temperatures T_V , T_{max} , and T_{min} near the critical pressure. The first two temperatures approach each other, as well as decrease with increasing pressure.

To explicitly demonstrate the evolution of the Verwey transition with pressure, we plot (Fig. 2) the $T_V(p)$ dependence by combining our magnetic susceptibility results and the resistivity data taken from Ref. 4. In the inset we redraw the data on a doubly logarithmic scale for both the almost perfectly stoichiometric ($\text{Fe}_3\text{O}_{4.002}$) and the slightly nonstoichiometric ($\text{Fe}_3\text{O}_{4.007}$) samples to demonstrate the exponential fit quality, as well as to show the difference between the two cases. We observe a clear exponential behavior of $T_V(p) = A(1 - p/p_c)^\nu$ above 3.5 GPa for the stoichiometric sample, with the critical pressure $p_c \simeq 8$ GPa and the value of the exponent $\nu \simeq 1/3$. Actually, the $\rho(T)$ data of Môri et al.⁴ already shows metallic conductivity at $p = 7.9$ GPa down to about 2 K, but a percent inaccuracy in determining p_c is acceptable given the inaccuracy of determining T_V for $p \gtrsim 7$ GPa. As the data in the inset shows, both p_c and ν depend strongly on the sample stoichiometry. For example, for $\delta = 0.007$ we have $p_c \simeq 6.1$ GPa and the critical exponent is reduced to the value $\nu \simeq 1/6$. This means that the nonstoichiometry is *not* equivalent to a reduction of critical pressure.

The nature of the metallic state (M) above p_c should be characterized in greater detail. This is particularly

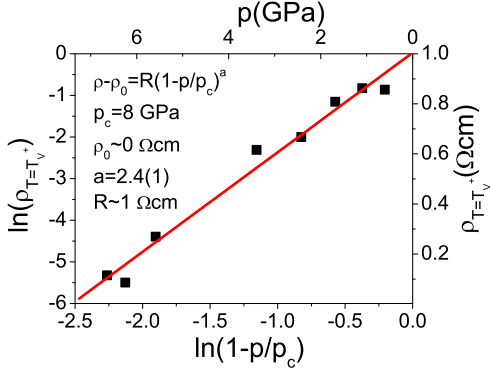


FIG. 3: Pressure dependence of the electrical resistivity just above the Verwey transition⁴ (at $T = T_{V+}$). The residual resistivity obtained from the fit is $\rho_0 \simeq 0$ within the fitting error.

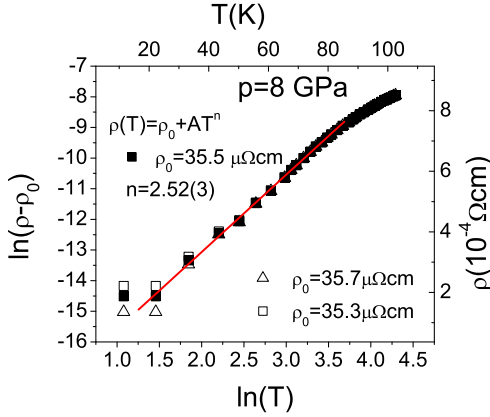


FIG. 4: Temperature dependence of electrical resistivity $\rho(T) = \rho_0 + AT^n$ of $\text{Fe}_3\text{O}_{4.002}$ at $p_c = 8$ GPa. The solid line (red online) corresponds to $\rho_0 = 35.5 \mu\Omega\text{cm}$ and $n = 2.52$. Open symbols show the sensitivity of the fits to ρ_0 value: slight variations of the ρ_0 value do not appreciably change the fitting accuracy.

important because for $p < 7.5$ GPa the state above T_V is clearly a semiconductor. A similar type of behavior to that exhibited in Fig. 2, though without any reference to *quantum critical behavior*, was suggested by Rosenberg et al.¹² Also, the magnetic susceptibility and the resistivity discontinuities in Fig. 2 follow the same dependence $T_V(p)$.

To provide quantitative evidence that we observe a criticality near the $T_{crit} = 0$, $p = p_c$ point, one requires a proper definition of the order parameter, as well as its dependence on $p - p_c$. In the previous studies of criticality near the insulator-metal transition^{5,7} the role of the order parameter was played by the conductivity difference $\sigma(p) - \sigma(p_c)$ or equivalently, directly by the resistivity.⁹ The two transport quantities mimic

the essential difference between carrier concentrations on both sides of the electronic transition in the equilibrium state. Additional evidence is provided by the behavior of physical quantities near p_c . For that purpose, our data from Fig. 1 is not directly useful, as the susceptibility is continuous upon approaching the system metallization. This in turn means, that magnetism is robust under the applied pressure, as no clear signature of *critical magnetic behavior* has been observed up to 300 K. In view of that circumstance, we reanalyzed the data of Móri et al.⁴ and plot in Figs. 3 and 4, respectively, the resistivity $\rho(T_{V+})$ just above the Verwey transition as a function of $p - p_c$, as well as $\rho(T)$ at p_c . We observe that, in the former situation we have roughly the scaling $\rho(p) = R[(p_c - p)/p_c]^a$, with $R \simeq 1 \Omega\text{cm}$ and $a \simeq 5/2$, whereas at $p = p_c$: $\rho(T) = \rho_0 + AT^n$, where $\rho_0 \simeq 35.5 \mu\Omega\text{cm}$, and $n \simeq 5/2$. These results differ from those for Mott-Hubbard systems^{5,7,9} obtained when the critical temperature $T_{crit} > 0$. However, it should be underlined again that, as only in the present case $T_{crit} = 0$, we are dealing with a true quantum critical regime for $p \rightarrow p_c$.

In Fig. 5 we plot the temperature dependence of the resistivity in the metallic phase (for $p = 9$ GPa). The resistivity $\rho(T)$ is roughly proportional to T^3 and the value of the residual resistivity is considerably reduced. The reduction of ρ_0 upon further metallization means that scattering on charged impurities (Fe^{2+} or Fe^{3+} vacancies) is reduced, since they are screened more effectively with increasing pressure. Note also the extreme sensitivity of the fitting upon the choice of the ρ_0 value. Parenthetically, this sensitivity may be regarded as an additional criterion of the sample quality.

The well defined exponential behavior of both the pressure and temperature dependencies of the resistivity match neither those observed near the quantum critical point for a ferro- and antiferro-magnetic system,¹³ nor those mentioned here for the antiferromagnetic systems near the critical point for the Mott-Hubbard transitions.^{5,7,9} In other words, the metallization of Fe_3O_4 represents a separate universality class of phase transitions. In connection, it would be very interesting to compare them in detail with those⁹ for the spin-canted antiferromagnet NiS_2 , a Mott-Hubbard insulator at $p = 0$, for which the Hund's rule also plays as an important role as for the ferrimagnetic state of Fe_3O_4 .

A basic question of relating the observed metallization to the microscopic properties of the system remains. On phenomenological grounds, one can relate the thermodynamics of the transition to the charge-order transition in the octahedral sites, connected with the freezing of the resonating electron between Fe^{3+} - Fe^{2+} configurations of the two ions at T_V .¹⁴ Considering the extra electron ($\text{Fe}^{2+} = \text{Fe}^{3+} + e^-$) as undergoing Mott-Wigner localization,¹⁵ one can write down a phenomenological Ginzburg-Landau functional, albeit with a fermionic form of the configurational entropy for the spinless (i.e. strongly polarized) fermions, and rationalize a

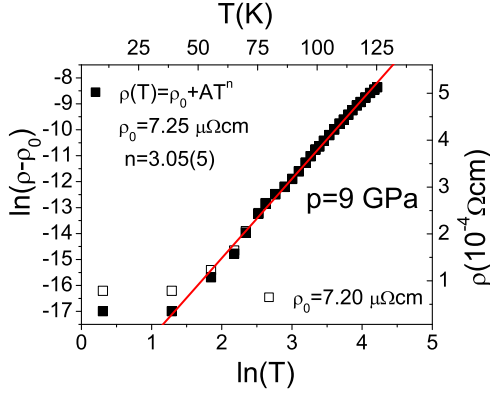


FIG. 5: Temperature dependence of resistivity $\rho(T) = \rho_0 + AT^n$ in the metallic (M) regime for $\text{Fe}_3\text{O}_{4.002}$. The solid line corresponds to $\rho_0 = 7.25 \mu\Omega\text{cm}$ and $n = 3.05$. The fitting accuracy does not change under a minute change of ρ_0 , as shown.

changeover from the first- to second-order upon varying the system stoichiometry.³

In recent years the above picture was investigated using spectroscopic methods.¹⁶ A pressure induced transformation from the inverse to the normal spinel structure was claimed to occur.¹⁷ This seems to be difficult to reconcile with the fact, that a transformation of this type should also take place at $p = 0$, which is not observed. In other words, the point $T_V(p = 0)$ should become also a terminal point of the first-order line $T_V(p)$. Nevertheless, in spite of the complications of the situation, in which both strong electronic correlations and electron-lattice coupling are important, a partial charge ordering was detected by X-ray scattering.¹⁸ This last result means, that strong correlations may play a primary role in the transition. This is because a relatively simple exponential behavior of $T_V(p)$, $\rho(T, p_c)$, and $\rho(T, p > p_c)$ means, that the underlying mechanism of the transition should be relatively simple physically. Otherwise, the change of T_V from above 120 K to zero should be sizably influenced by e.g. the difference in thermal occupation of the low-energy phonons and hence lead to nonuniversal

behavior.

Having in mind the underlying simplicity of the electronic correlations as the primary force, we can easily rationalize the $T_V \sim (p_c - p)^{1/3}$ dependence. Namely, regarding strongly correlated polarized $3d$ electrons as *spinless fermions*, we can write down the Landau free energy of the electronic system in the form^{3,14}

$$F = F_0 + E(\Psi) - k_B T [\Psi \ln(\Psi/2) + (1 - \Psi) \ln(1 - \Psi)]$$

$$\approx F'_0 + a(T - T_V)\Psi + b\Psi^2 + \dots, \quad (1)$$

where $E(\Psi) = \epsilon_0 + \epsilon_1\Psi + \epsilon_2\Psi^2 + \dots$ is the system energy, the third term the relative fermionic entropy, Ψ is the density of itinerant electrons (resonating $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ electrons in the octahedral sites), and ϵ_0, \dots, b are constants. The coupling of the electron subsystem to the lattice introduces an additional term of the Holstein type $\lambda\Psi\Delta x/a = \lambda\Psi(\Delta V/V)^{1/3}$, where $\Delta x/a$ and $\Delta V/V$ are respectively, the relative lattice-parameter and volume changes under pressure, and λ is the local electron-lattice coupling constant. Assuming that, $\epsilon_1 \sim \lambda(\dots)$ and since¹² $\Delta V \sim p_c - p$, the change of T_V induced by applied pressure is $T_V = \lambda'(p_c - p)^{1/3}$, which is in agreement with what we observed.

In summary, we have demonstrated, that the metallization of magnetite under pressure can be described by a simple exponential scaling of physical properties, including the transition temperature T_V , the resistivity near the critical pressure $\rho(p, T_{V+})$ at the transition, and as a function of temperature, $\rho(p = p_c, T)$, at p_c and above. These properties provide direct evidence of critical behavior with a quantum critical point at $p_c \approx 8$ GPa. It is also suggested, that the strong electronic correlations lead to a partial charge order (and concomitant with it partial localization) and may be the source of the observed volume change, as is the case for Mott-Hubbard systems.

The work was supported by the Grants Nos. 1 P03B 001 29 and 1 P03B 01 530 from the Ministry of Science and Higher Education. The work has been carried out partly within the COST P-16 European Project. We thank also George Honig for discussion.

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